



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

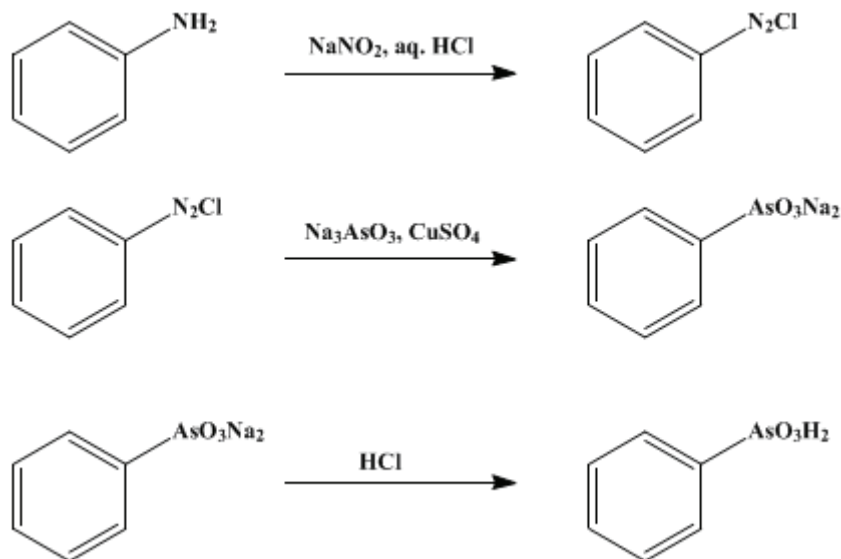
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## PHENYLARSONIC ACID

### [Benzenearsonic acid]



Submitted by R. H. Bullard and J. B. Dickey.  
Checked by W. H. Carothers and W. L. McEwen.

### 1. Procedure

In a 12-l. round-bottomed flask fitted with a mechanical stirrer is placed 1 l. of water. The water is heated to boiling, and 500 g. (4.7 moles) of anhydrous sodium carbonate is added. As soon as the carbonate has dissolved, 250 g. (1.26 moles) of arsenious oxide and 11 g. of crystalline copper sulfate are added with stirring. When all the solids have dissolved the solution is cooled with stirring under a stream of tap water until the temperature falls to  $15^\circ$ .

Concurrently with the preparation of the sodium arsenite solution, a solution of benzenediazonium chloride is prepared. To a well-stirred mixture of 186 g. (2 moles) of technical aniline, 400 cc. (4.8 moles) of concentrated hydrochloric acid (sp. gr. 1.19), 1 l. of water, and enough crushed ice to make a volume of about 3 l., is added slowly a solution of 145 g. (2 moles) of 95 per cent sodium nitrite in 500 cc. of water. This requires about thirty to forty minutes.

The benzenediazonium chloride solution is then added with stirring during a period of one hour to the suspension of sodium arsenite, cooled in an ice and salt bath to  $0^\circ$ . The temperature during the reaction is held below  $5^\circ$  (Note 1). Frothing takes place owing to the escape of nitrogen, but this is easily controlled by the occasional addition of a small quantity of benzene. Stirring is continued for one hour after the addition of the diazonium chloride solution, and the mixture is filtered to remove the solid material which separates. This is washed with 500 cc. of cold water, and the combined liquors are concentrated over a free flame to a volume of about 1.5 l. (Note 2).

To the hot concentrated solution, which is deep brown in color, concentrated hydrochloric acid is added until no more tarry material separates (Note 3). The tar is filtered and more hydrochloric acid is added until, after filtering, a clear pale yellow solution results. It is important to remove all the tar at this time; otherwise, subsequent recrystallizations will not free the product from color. The phenylarsonic acid is then precipitated by the addition of 250 cc. of concentrated hydrochloric acid (sp. gr. 1.19) (Note 4). When the mixture has cooled (preferably by standing overnight) the phenylarsonic acid is filtered on a Büchner funnel and washed with 200 cc. of cold water. The light yellow crystals are dissolved in 500 cc. of boiling water, 20 g. of Norite is added, the solution filtered hot, and the filtrate allowed to cool.

After filtering and drying, the white crystals melt with decomposition at 154–158°, passing into the anhydride, C<sub>6</sub>H<sub>5</sub>AsO<sub>2</sub>. The yield is 160–182 g. (39–45 per cent of the theoretical amount) (Note 5).

## 2. Notes

1. This temperature is advised because it appears to be near the optimum with regard to yield and ease of purifying the product. However, a reaction temperature as high as 15° may be used with good results.
2. The solution is concentrated at atmospheric pressure since frothing occurs if reduced pressure is used.
3. About 100 cc. of hydrochloric acid is required. Care must be exercised not to precipitate any of the phenylarsonic acid.
4. Too large an excess of hydrochloric acid will dissolve some of the product and lower the yield.
5. In occasional runs by this procedure yields as high as 57 per cent have been obtained, but the reasons for this are not known.

## 3. Discussion

Phenylarsonic acid has been prepared by oxidizing phenyldichloroarsine<sup>1</sup> or phenyldiiodoarsine<sup>2</sup> with chlorine in water; by the oxidation of phenylarsine with nitric acid or air;<sup>3</sup> by decomposing phenylarsinetetrachloride or phenylarsineoxychloride with water;<sup>4</sup> by heating iodobenzene or bromobenzene with potassium arsenite;<sup>5</sup> by diazotizing *p*-arsanilic acid and decomposing in a solution of sodium hydrosulfite and hydrochloric acid;<sup>6</sup> by the action of potassium arsenite on potassium benzeneisodiazoxide;<sup>7</sup> by the action of benzenediazonium chloride on sodium arsenite in the presence of a copper compound<sup>8</sup> or of magnesium chloride and copper powder;<sup>9</sup> and by the action of a neutral or alkaline mixture containing arsenious oxide, a copper salt, and a reducing agent on benzenediazonium chloride.<sup>10</sup>

The preparation given here in detail is essentially that described by Palmer and Adams.<sup>8</sup> It has been reported that the use of buffers to ensure constant *pH* increases the yield of phenylarsonic acid in this reaction.<sup>11</sup>

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## References and Notes

1. Michaelis and Loesner, Ber. **27**, 265 (1894); Rosenheim and Bilecki, *ibid.* **46**, 551 (1913); Roeder and Blasi, *ibid.* **47**, 2752 (1914).
2. Bertheim, *ibid.* **47**, 274 (1914).
3. Palmer and Dehn, *ibid.* **34**, 3599 (1901); Dehn, Am. Chem. J. **33**, 149 (1905).
4. Michaelis, Ber. **10**, 625 (1877); LaCoste and Michaelis, Ann. **201**, 203 (1880).
5. Dehn, Am. Chem. J. **33**, 140 (1905); Rosenmund, Ber. **54**, 438 (1921).
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9. Bart, Ger. pat. 254,092 [Fr. **11**, 1030 (1912-14)].
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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

arsenious oxide

potassium benzeneisodiazoxide

copper compound

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

aniline (62-53-3)

nitric acid (7697-37-2)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

copper sulfate (7758-98-7)

benzenediazonium chloride,  
benzenediazonium chloride

sodium nitrite (7632-00-0)

sodium hydrosulfite (7775-14-6)

copper powder (7440-50-8)

p-Arsanilic acid (98-50-0)

sodium arsenite

Norite (7782-42-5)

chlorine (7782-50-5)

bromobenzene (108-86-1)

Iodobenzene (591-50-4)

Phenylarsonic acid,  
Benzeneearsonic acid (98-05-5)

phenyldichloroarsine (696-28-6)

phenyldiiodoarsine (6380-34-3)

phenylarsine

phenylarsinetetrachloride

phenylarsineoxychloride

potassium arsenite

magnesium chloride (7786-30-3)

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